

Attorney Docket No. 29462-025

**IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)**

Patent Application of : **Jutta KLÖWER, et al.**  
Int'l Application No. : **PCT/EP97/06592**  
Int'l Filing Date : **November 26, 1997**  
Priority Date : **January 29, 1997**  
Title of the Invention : **AUSTENTIC NICKEL-CHROMIUM-  
MOLYBDENUM-SILICON ALLOY  
WITH HIGH CORROSION  
RESISTANCE TO HOT CHLORIDE-  
CONTAINING GASES AND  
CHLORIDE**

**TRANSMITTAL  
LETTER TO  
UNITED  
STATES  
DESIGNATED/  
ELECTED  
OFFICE  
(DO/EO/US)**

"Express Mail" mailing label number

EJ85397125605

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated below and is addressed to: Hon. Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Date of Deposit July 28, 1999

(Signature) \_\_\_\_\_



Hon. Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Sir:

Applicant(s) respectfully submit(s) the following items for entry of the above-identified international application into the national phase:

- (1) ☒ This express request to immediately begin national examination procedures under 35 U.S.C. §371 of the application.
- (2) ☒ The Commissioner is hereby authorized to deduct the large entity fee of \$880.00 from deposit account number 16-2500 of the undersigned:  
  
☒ basic National fee pursuant to 37 CFR 1.492(a)(5)  
(filing with EPO or JPO search report)

☐ basic National fee pursuant to 37 CFR 1.492(a)(3)  
(neither IPEA nor ISA fee paid to USPTO)

☐ surcharge for late filing of National fee or  
Oath/Declaration

☐ \_\_\_ independent claims in excess of 3  
\_\_\_ claims in excess of 20  
\_\_\_ multiple dependent claims

☐ 1/2 reduction for filing by small entity

☐ surcharge - late filing of English translation

☒ fee for recording the enclosed Assignment

(3) ☒ A copy of the originally filed international application (in German and English).

(4) ☒ A copy of the international application as published (in German and English).

(5) ☒ A copy of the substitute pages (in German) of the application.

(6) ☒ A translation into English of substitute pages of the application.

(7) ☒ Declaration and Power of Attorney.

(8) ☒ A copy of the International Preliminary Examination Report (in German).

(9) ☒ Information Disclosure Statement.

(10) ☒ PTO-1449 form and listed references.

(11) ☒ Assignment Document.

(12) ☒ A copy of the International Search Report (in English).

(13) ☒ Preliminary Amendment.

(14) ☒ Other: Office Action from the German Patent Office dated August 7, 1997 (in German and English).

(15) The above checked items are being transmitted:

- (a) ☐ before the 18th month publication.
- (b) ☐ after publication and the Article 20 communication but before 20 months from the priority date.
- (c) ☐ after 20 months but before 22 months.
- (d) ☐ after 22 months.
- (e) ☒ by 30 months and a proper demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

If any fee submitted at any time in this case be found insufficient, please debit the balance to the Patent Office Account No. 16-2500 of the undersigned; if any other deficiency in the papers submitted be found that may result in a delayed filing date, please notify the undersigned attorney by telephone at (212) 969-3000.

Respectfully submitted,  
PROSKAUER ROSE LLP  
Attorneys for the Applicant(s)

By: Charles Guttman  
Charles Guttman  
Reg. No. 29,161

Date: July 28, 1999

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Jutta KLÖWER, et al.  
Int'l Appl. No. : PCT/EP97/06592  
U.S. Filing Date : Concurrently  
U.S. Serial No. :  
Title : AUSTENITIC NICKEL-CHROMIUM-  
MOLYBDENUM-SILICON ALLOY  
WITH HIGH CORROSION  
RESISTANCE TO HOT CHLORIDE-  
CONTAINING GASES AND  
CHLORIDE

#13/a  
1-8-00  
**PRELIMINARY  
AMENDMENT  
TO REMOVE  
MULTIPLE  
DEPENDANT  
CLAIMS**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the claims of the above-identified patent application to remove all multiple dependencies as follows:

Claim 5, please delete "one of the claims 1 to 4" and insert --claim1--;

Claim 6, please delete "one of the claims 1 to 4" and insert --claim 1--;

Claim 7, please delete "one of the claims 1 to 4" and insert --claim 1--.

**REMARKS**

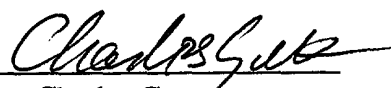
Amendments are being made to the claims to remove their multiple dependencies.

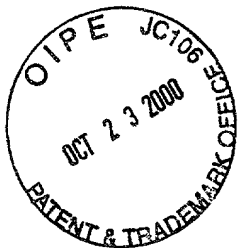
Please proceed to examine the application as amended herein.

Respectfully submitted,  
PROSKAUER ROSE LLP  
Attorneys for Applicant(s)

Date: July 28, 1999

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1742  
Attorney Docket No. 29462-025

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Group Art Unit : 1742  
Examiner : Andrew L. Oltmans

Applicant : Jutta KLÖWER, et al.  
Serial No. : 09/355,422  
Filing Date : July 28, 1999  
Entitled : AUSTENITIC NICKEL-CHROMIUM-  
MOLYBDENUM-SILICON ALLOY WITH  
HIGH CORROSION RESISTANCE TO  
HOT CHLORIDE-CONTAINING GASES  
AND CHLORIDE

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AMENDMENT

I hereby certify that this paper is being deposited this date with the U.S. Postal Service as first class mail addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

*Michael A. Hart* October 20, 2000

668260 2249560  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

RECEIVED  
OCT 30 2000  
TC 1700 MAIL ROOM  
In response to the Office Action dated April 20, 2000, please amend the above-identified patent application as follows:

IN THE SPECIFICATION

Please amend the specification as indicated below.

Page 1, after the title, please insert --BACKGROUND OF THE INVENTION--.

Page 1, line 13, please delete "niob" and replace it with --niobium--.

Page 1, line 18, please delete "losses" and replace it with --loss--.

Page 2, line 15, after " $\text{Si} \leq 2$ " please insert --%--.

Page 2, line 16, please delete "Niob" and replace it with --niobium--.

Page 2, line 17, please delete "Titan" and replace it with --titanium--.

Page 3, before line 1, please insert --SUMMARY OF THE INVENTION--.

Page 4, line 14, please delete "0.15%" and replace it with --0.015%--.

Page 4, line 24, please delete "0.001 - 0.001 %" and replace it with --0.001 - 0.01%--.

Page 5, after line 10, please insert:

--BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1-5 are bar graphs depicting various characteristics of the alloy in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION--.

Page 5, line 19, and page 6, line 12, please delete "2,4856" and replace it with --2.4856--.

Page 5, line 20, please delete "and" and replace it with --to--.

Page 8, line 11, please delete "phosphor" and replace it with --phosphorus--.

IN THE CLAIMS

Please cancel claims 1-7 without prejudice and substitute the following claims therefor:

B<sub>1</sub> --8. Austenitic nickel-chromium-molybdenum alloys with additions of silicon, consisting essentially of (in mass percentages):

Chromium:	18 to 22%
Molybdenum:	6 to 10%
Silicon:	0.6 to 1.7%
Carbon:	0.002 to 0.05%
Iron:	1 to 5%
Manganese:	0.05 to 0.5%
Aluminum:	0.1 to 0.5%
Titanium:	0.1 to 0.5%
Magnesium:	0.005 to 0.05%
Calcium:	0.001 to 0.01%
Vanadium:	max. 0.5%
Phosphorus:	max. 0.02%
Sulphur:	max. 0.01%
Boron:	0.001 to 0.01%
Copper:	max. 0.5%
Cobalt:	max. 1%
Niobium:	max. 0.5%
Hafnium:	0.02 to 0.5%

balance nickel and residual impurities wherein the total amount of Nb + Al + Ti does not exceed 1%.

9. Austenitic nickel-chromium-molybdenum alloys with additions of silicon, consisting essentially of (in mass percentages):

Chromium:	18 to 20%
Molybdenum:	8 to 9%
Silicon:	0.7 to 1.1%
Carbon:	0.002 to 0.015%
Iron:	2.5% to 3.5%
Manganese:	0.05 to 0.1%
Aluminum:	0.1 to 0.3%
Titanium:	0.1 to 0.4%

Magnesium:	0.005 to 0.15 %
Calcium:	0.001 to 0.005 %
Vanadium:	max. 0.1 %
Phosphorus:	max. 0.002 %
Sulphur:	max. 0.001 %
Boron:	0.001 to 0.01 %
Copper:	max. 0.5 %
Niobium:	max. 0.5 %
Hafnium:	0.03 to 0.06 %

balance nickel and other impurities.

- 662240 "continued"
10. The alloy of claim 8, wherein the molybdenum content is in the range of 6.5 to 9.5 % by mass.
  11. The alloy of claim 8, wherein the silicon content is in the range of 0.6 to 1.3 % by mass.
  12. Pipes, sheet metal, band material, foils, wires, and items made from these semi-products, made from the alloy of claim 8.
  13. Pipes made from at least two metals wherein one of said metals is the alloy of claim 8.
  14. A corrosion protection material made from the alloy of claim 8.--

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#### IN THE ABSTRACT

Please add the Abstract submitted on the attached separate page.



**REMARKS**

Reconsideration of the above-identified patent application, as amended herein, is respectfully requested.

This Amendment is in response to the Office Action dated April 20, 2000. Claims 1-7 have been rejected. Claims 1-7 are canceled herein and replaced with new claims 8-14. Of the foregoing, only claims 8 and 9 are independent.

A Substitute Translation of the International Application, including the Amendments of April 16, 1999 made during the International Phase, is enclosed herewith. It appears that a page from the Verified Translation filed on July 28, 1999, may have been inadvertently excluded. It appears that the translation of page 7 of the German language application was inadvertently excluded. No new matter has been added because the German language application entered the National Phase on July 28, 1999, with this page included. The Amendments made herein to the specification, and the references to certain locations in the specification, refer to the page/line numbering of the Substitute Translation.

Although the disclosure has not been objected to by the Examiner, the specification is amended to correct typographical errors, and to provide headings in accordance with accepted

practice. An Abstract is also submitted to conform with the requirements set forth in 37 CFR 1.72 and MPEP 608.01(b). No new matter has been added.

Claims 5-7 have been rejected under 35 U.S.C. §101 as being directed to non-statutory subject matter. Claims 6 and 7 have also been rejected under 35 U.S.C. §112, second paragraph, for not particularly pointing out and distinctly claiming the subject matter of the invention. Claims 5 -7 are canceled herein and replaced with new claims 12-14. The new claims were drafted with consideration of the various informalities noted in the Office Action, and which are now believed to overcome the rejections under 35 U.S.C. §112, second paragraph, and the rejection under 35 U.S.C. §101. Accordingly, it is requested that these rejections be withdrawn.

Claims 1 and 3-7 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Kondo et al. (US Patent 4,110,110), and claims 1-7 have been rejected as being unpatentable over German Patent 1,233,609. Claims 1-7 are canceled herein and replaced with new claims 8-14 which are directed generally to the subject matter previously presented in the canceled claims, and rewritten in clean claim form for the Examiner's convenience. For a rejection under 35 U.S.C. §103(a) to be sustained, the differences between the features of the references and the present invention must be obvious to one skilled in the art.

New claim 8 recites:

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"8. Austenitic nickel-chromium-molybdenum alloys with additions of silicon, *consisting essentially of* (in mass percentages):

Chromium:	18 to 22%
Molybdenum:	6 to 10%
<b>Silicon:</b>	<b>0.6 to 1.7%</b>
Carbon:	0.002 to 0.05%
Iron:	1 to 5%
Manganese:	0.05 to 0.5%
Aluminum:	0.1 to 0.5%
Titanium:	0.1 to 0.5%
Magnesium:	0.005 to 0.05%
Calcium:	0.001 to 0.01%
Vanadium:	max. 0.5%
Phosphorus:	max. 0.02%
Sulphur:	max. 0.01%
Boron:	0.001 to 0.01%
Copper:	max. 0.5%
Cobalt:	max. 1%
Niobium:	max. 0.5%
<b>Hafnium:</b>	<b>0.02 to 0.5%</b>

balance nickel and residual impurities wherein the total amount of Nb + Al + Ti does not exceed 1%."

Kondo et al. disclose a nickel-based alloy containing similar components but do not disclose the presence of 0.6 to 1.7 % silicon. In contrast, Kondo et al. disclose a silicon content of 0.05 to 0.5%, which is preferably within the range of 0.05 to 0.2%. See column 3, line 17, and column 4, line 28. Although Kondo et al. do disclose the presence of silicon in their alloy, Kondo et al. limit the amount of silicon to the above-noted amounts to prevent spalling of the oxide film and to inhibit the occurrence of selective oxidation of grain boundaries. See column 4, lines 56-59.

Specifically, Kondo et al. teach a minimum of 0.05% and a **maximum of 0.5%** silicon. Kondo et al. expressly teach that a silicon content over the maximum of 0.5% causes the undesirable effect of the occurrence of "whisker crystals" in the alloy. See column 2, lines 52-64. Kondo et al. teach that an alloy which is easily susceptible to these whisker crystal is substantially wearable by high-temperature oxidation, and often causes contamination of surrounding parts. See column 5, lines 5-10, especially lines 9-10 which recite:

"Silicon content should not therefore be over 0.5%, preferably not over 0.2%."

Column 11, lines 46-51 of Kondo et al. recite:

"...when the silicon content exceeds 0.1%, growth of whisker crystals becomes apparent, and this trend becomes more remarkable as the silicon content increases. In view of the foregoing, when the other characteristics are ignored, the **least possible silicon content** is desirable."

The silicon content taught in Kondo et al. is in stark contrast to the present invention which discloses an alloy which has 0.6 to 1.7% silicon. This is **well above** the range taught by Kondo et al. The present invention requires, in accordance with new claim 8, a **minimum** of 0.6% silicon to produce the desired results of high corrosion resistance to chloride and sulfate corrosion. See the specification, page 6, the entire page.

It would therefore not have been obvious to one of ordinary skill in the art to include silicon in the range of 0.6 to 1.7% by reading Kondo et al., as Kondo et al. teach away from a silicon content greater than 0.5%.

Kondo et al., not being limited to the preferred embodiments, but rather being considered as a whole, **do not** teach a silicon content greater than 0.5%, as required by claim 8 of the present invention. Therefore, Kondo et al. do not render the present invention obvious.

Furthermore, the present invention requires, according to new claim 8, the presence of 0.02 to 0.5% hafnium. Hafnium is included in the alloy of the present invention to improve adherence of protective oxide layers in case of rapid temperature changes, specifically in automobile exhaust systems. See the specification, page 7, lines 10-13.

Nowhere do Kondo et al. disclose or teach an alloy having 0.02 to 0.5% hafnium. In contrast, Kondo et al. are silent in this regard. The alloy of Kondo et al. "consists essentially of" the components listed in column 3, lines 7-26. Components having any essential significance to the combination, other than those listed, are therefore **excluded** from the combination. As hafnium has an essential significance to the alloy of the present invention, it would not have been obvious for one skilled in the art, by reading Kondo et al., to include 0.02 to 0.5% hafnium in the alloy.

Furthermore, new claim 8 **consists essentially of** the elements recited therein. As noted above, the term "consisting essentially of" excludes components having any essential significance from the combination. Therefore, new claim 8 excludes the presence of tungsten in the alloy. In contrast, Kondo et al. **require** 0.1 to 25% tungsten. Tungsten has significance in the alloy and is included to "intensify the solid-solution with a view to improving the mechanical properties and the workability of Ni-Cr alloys...." See column 1, lines 63-65.

In contrast, tungsten is excluded from the alloy according to the present invention because it is known by one skilled in the art to have negative effects on the claimed alloy. Tungsten is known to initiate precipitation of intermetallic phases, and lead to brittleness, or loss of ductility. The amounts of aluminum, titanium, and niobium are limited to 1% in the invention for the same reason. See the specification, page 8, lines 1-3. Furthermore, it is known that tungsten included in the inventive alloy will have a negative effect on the corrosion resistance of the alloy. For these reasons, the element tungsten is **excluded** from the invention, as claimed in claim 8, by use of the language "consisting essentially of."

German Patent 1,233,609 ('609) discloses a nickel chromium alloy consisting of similar components. However, the invention, as recited in claim 8, contains the elements recited in much more restricted quantities than those disclosed in '609. Specifically, the present invention limits the range of chromium to 18 to 22%, wherein '609 teaches a very wide range of 5 to 30%. See

the specification, page 7, lines 5-7 which recite: "The chromium content of the alloy according to the invention should be between 18% and 22% in order to ensure sufficient corrosion resistance. Greater contents in chromium render the workability of nickel-chromium-molybdenum alloys markedly more difficult." Therefore, the claimed invention **cannot** contain over 22% chromium, as allowed by '609.

Furthermore, the present invention limits the range of molybdenum to 6 to 10%, wherein '609 teaches a very wide range of 0 to 15%. Molybdenum is a very important component of the present invention, in the amounts recited, to obtain the desired characteristics of the inventive alloy. See the specification, page 7, lines 1-4, which state that the **minimum** amount of molybdenum of 6% is **required** "in order to avoid wet corrosion in case of a drop below the dew point." The maximum amount of molybdenum is also very specific, and is limited to 10%. This is "because, as shown in Fig. 4, the vulnerability to sulphate corrosion increases with molybdenum contents." See the specification, page 7, lines 1-4.

In contrast, '609 teaches the very broad range molybdenum content of 0 to 15%. Although the range of molybdenum disclosed in '609 overlaps the molybdenum content disclosed in the present invention, '609 may **exclude** the presence of molybdenum in the alloy. A content of 0% is taught by this reference. This is in contrast to the present invention which discloses a molybdenum content of **at least 6%** to obtain the desired characteristics of the inventive alloy.

Still further, the present invention limits the range of iron, in accordance with claim 8, to 1 to 5%, wherein '609 teaches a wider range of 0 to 5%. Iron is a very important component of the present invention, in the amounts recited, to obtain the desired characteristics of the alloy. See the specification, page 7, lines 15-18, which state that the **minimum** amount of iron **required** by the invention is 1% "to ensure the workability of the alloy." A maximum of 5% of iron is disclosed "as the danger that slightly volatile iron chlorides may be produced exists in case of higher iron contents in chloride-containing media." (Page 7, lines 15-18.)

In contrast, '609 teaches the range of iron may be from 0 to 5%. Although the range of iron disclosed in '609 overlaps the iron content disclosed in the present invention, '609 may **exclude** the presence of iron in the alloy. A content of 0% is taught by this reference. This is in contrast to the present invention which discloses an iron content of **at least 1%** to obtain the desired characteristics of the inventive alloy.

According to the specification, at page 6:

"The outstanding characteristics of the alloy according to the invention can be attributed to the silicon additions and to the coordination of the alloy elements molybdenum, chromium and iron."



The inventive alloy therefore discloses specific minimum and maximum ranges of silicon, molybdenum, chromium, and iron. The alloy taught by '609 may only contain chromium; molybdenum, silicon, and iron may be **excluded** from the combination.

Accordingly, it is respectfully submitted that new claim 8 is not rendered obvious by either Kondo et al. or German Patent No. 1,233,609. As new claims 10-14 depend from new claim 8, it is believed that they too are not rendered obvious by either Kondo et al. or '609. It is respectfully submitted that the rejection under 35 U.S.C. §103(a) thereto be withdrawn.

New claim 9 corresponds to canceled claim 2, which has been rejected as being obvious over DE 1,233,609. New claim 9 relates to a preferred embodiment of the invention and contains similar components to the alloy of claim 8, but are somewhat restricted. Specifically, claim 9 restricts the contents of chromium, molybdenum, silicon, and iron, even further than claim 8, as follows:

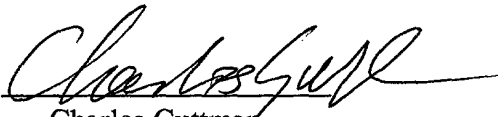
	Claim 8	Claim 9
Chromium	18 to 22%	18 to 20%
Molybdenum	6 to 10%	8 to 9%
Silicon	0.6 to 1.7%	0.7 to 1.1%
Iron	1 to 5%	2.5 to 3.5%

Furthermore, the alloy of claim 9 also contains a more restricted amount of hafnium (0.03 to 0.06%) than the range disclosed in claim 8. For the reasons discussed above with regard to claim 8, it is also believed that claim 9 is not rendered obvious by DE 1,233,609. Specifically, the present invention requires specific limited contents of chromium, silicon, molybdenum, and iron to achieve the desired characteristics of the alloy. These ranges are much more specific than those taught by '609, as noted above.

Accordingly, it is respectfully submitted that new claim 9 is not rendered obvious by DE 1,233,609. It is respectfully submitted that the rejection under 35 U.S.C. §103(a) thereto be withdrawn.

In light of the foregoing amendments and arguments, the application is now believed to be in proper form for allowance of all claims and a notice to that effect is earnestly solicited.

Respectfully submitted,  
PROSKAUER ROSE LLP  
Attorneys for Applicant(s)

By   
Charles Guttman  
Reg. No. 29,161

Date: October 20, 2000

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Enclosure: Substitute Translation

658220 "22492660

DEPT. OF THE INTERIOR  
BUREAU OF LAND MANAGEMENT  
WASHINGTON, D. C. 20250

An austenitic nickel-chromium-molybdenum alloy with additions of silicon, has the following components (in mass percentages): 18 to 22% chromium, 6 to 10% molybdenum, 0.6 to 1.7% silicon, 0.002 to 0.05% carbon, 1 to 5% iron, 0.05 to 0.5% manganese, 0.1 to 0.5% aluminum, 0.1 to 0.5% titanium, 0.005 to 0.05% magnesium, 0.001 to 0.01% calcium, a maximum of 0.5% vanadium, a maximum of 0.02% phosphorus, a maximum of 0.01% sulphur, 0.001 to 0.01% boron, a maximum of 0.5% copper, a maximum of 1% cobalt, a maximum of 0.5% niobium, 0.02 to 0.5% hafnium, balance nickel and residual impurities whereby the total amount of additions of Nb + Al + Ti does not exceed 1%.

Attorney Docket No. : 29462-025

Serial No. : 09/355,422

(Substitute Specification - Clean Version)

**AUSTENITIC NICKEL-CHROMIUM-MOLYBDENUM-SILICON ALLOY WITH  
HIGH CORROSION RESISTANCE TO HOT CHLORIDE-CONTAINING GASES AND  
CHLORIDE**

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66320" 243360

**[0001]** The invention relates to an austenitic nickel-chromium-molybdenum-silicon alloy with additions of silicon.

**[0002]** In plants and aggregates where hot chlorine-containing gases and chloride-containing deposits occur (chemical plants, thermal waste-disposal facilities, in particular when recycling special waste, plants for the recycling of biomass, large diesel engines, exhaust systems of automobiles) ferritic boiler construction steel is used at temperatures up to 400°C. At higher temperature, nickel-chromium-molybdenum alloys with 21.5% chromium, 9% molybdenum, 3.7% niobium 2.5% iron, and the remainder nickel and unavoidable impurities (German material number 2.4856) are used (steel code 1995)

**[0003]** The alloy with the material number 2.4856 is however difficult to process. In addition this alloy suffers a considerable ductility losses at temperatures above 500°C, a loss which may result in the formation of cracks in pressure-carrying components and/or those

subjected to heavy mechanical stress. To a certain extent, the start of precipitation of the ductility-reducing precipitation can be delayed by lowering the iron content.

[0004] Measures leading to a clear rise in ductility are indicated in the international patent application WO 95/31579 in which a new alloy is described on basis of the alloy according to material number 2.4856 which distinguishes itself through increased hot and cold formability and a greater ductility.

[0005] The new alloy described in this publication has still some disadvantages. Thus the indicated ductility-raising measures cause the corrosion resistance to gases containing great amounts of chlorine and coatings containing chloride to drop below that of alloy with the material number 2.4856. Already with this alloy, high corrosion rates occur for reasons constantly rising process and exhaust gas temperatures due to the increase in effectiveness. Alloys of the type 2.4856 are in addition subject to heat corrosion by sulphate-containing deposits, so that a considerable need for an alloy of a different type, with improved resistance to high-temperature corrosion exists.

[0006] JP-A 6199649 discloses an alloy for electrically conductive rollers whose essential alloy components (in weight percentages) are indicated as follows: Cr 15 - 30%, Mo 4 - 10%, Si  $\leq 2$  , Fe  $\leq 10$  %, Mn  $\leq 2$  %, Al 0.2 - 2 % and Ti 0.05 - 2 %. Alternatively, Niob can also

be used instead of Titan in the above-mentioned distribution.

[0007] WO-A 8901985 discloses a corrosion-resistant cast alloy which (in weight %) contains essentially the following alloy components: Cr 20 - 25 %, Mo 6 - 9 %, Si 0.5 - 1 %, Fe 15 - 20 % and Mn 2 - 4 %. In addition a high addition of Co, in the amount of 4 - 8% is indicated.

[0008] It is the object of present invention to develop an alloy with a resistance to chlorine gas corrosion and to chloride-containing coatings significantly superior to that of the state of the art, while at the same time providing increased resistance to sulphate corrosion while possessing high ductility over the entire temperature range up to 1000°C.

[0009] The object is attained by means of a silicon-containing nickel-chromium-molybdenum alloy which is made up of the following components (in mass %):

Cr	18 - 22 %
Mo	6 - 10 %
Si	0.6 - 1.7 %
C	0.002 - 0.05 %
Fe	1 - 5 %
Mn	0.05 - 0.5 %
Al	0.1 - 0.5 %
Ti	0.1 - 0.5 %
Mg	0.005 - 0.05 %

Ca 0.001 - 0.01 %

V max. 0.5 %

P max. 0.02 %

S max. 0.01 %

B 0.001 - 0.01 %

Cu max. 0.5 %

Co max 1 %

Nb max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.02 - 0.5%

the remainder being nickel and impurities caused by the melting process, whereby the total amount of additions in Nb + Al + Ti do not exceed 1 %.

**[0010]** Advantageous further developments of the object of the invention are to be found in the sub-claims.

**[0011]** The alloy according to the invention is clearly more high-temperature corrosion resistant to chlorine-containing gases, chloride-containing ash, deposits and salt compounds than those of the state of the art, while at the same time being corrosion resistant to sulphate corrosion and wet corrosion and is at the same time highly ductile.

**[0012]** A preferred alloy is composed of the following alloy components (in mass percentages) :



Cr	18 - 20 %
Mo	8 - 9.0 %
Si	0.7 - 1.1 %
C	0.002 - 0.15 %
Fe	2.5 - 3.5 %
Mn	0.05 - 0.1 %
Al	0.1 - 0.3 %
Ti	0.1 - 0.4 %
Mg	0.005 - 0.15 %
Ca	0.001 - 0.005 %
V	max. 0.1 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 - 0.001 %
Cu	max. 0.5 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.03 - 0.06%  
the remainder being nickel and impurities caused by the melting process.

[0013] The alloy is advantageously suited on the one hand for the production of pipes, in particular composite pipes, sheet metal, band material, foils, wires as well as items made from these semi-products, and is furthermore suitable as corrosion protection in form of applied welding or plating.

[0014] The advantageous characteristics of the alloy according to the invention appear in the following examples of embodiments. Table 1 shows for example analyses of batches of the alloy according to the invention (A-F) as well as the comparison alloys (G, H) other than the combination according to the invention (G, H). The alloy 2.4856 was used for comparison. All

alloy variants were produced from cast blocks by means of hot rolling followed by cold rolling at room temperature.

**[0015]** The resistance of the alloy according to the invention to chloride corrosion is depicted in Figs. 1 and 2. For the tests, polished and clean test coupons of different test alloys were submerged in an aqueous solution of 1 mol/l NaCl, 0.1 mol/l CaCl<sub>2</sub> and 0.25 mol/l NaHCO<sub>3</sub>, dried at 60°C and then aged in the air at 750°C for 240 hours. This test simulates the stresses which appear e.g. in exhaust systems of car engines (at bellows for uncoupling catalytic converter and engine). Fig. 1 shows the disappearance of metal, Fig. 2 shows the metallographically determined corrosion effect at the end of the test. In tests it was found surprisingly that the resistance to chloride corrosion could be markedly improved over that of alloy 2,4856 by the addition of silicon in quantities from 0.6 and 1.7%.

**[0016]** The advantageous influence of silicon can also be seen in Fig. 3 which shows the metallographically determined corrosion effect on samples which were aged in a complex medium (chlorine-containing synthetical waste combustion gas (2.5 g/m<sup>3</sup> HCl, 1.3 g/m<sup>3</sup> SO<sub>2</sub>/ 9% O<sub>2</sub>, the remainder N<sub>2</sub>) while at the same time adding chloride-containing boiler ash) for over 1000 hours at 600°C. By comparison with the low-silicon batch (e.g. G) the alloy containing silicon according to the invention suffered markedly less corrosion effect.

[0017] Fig. 4 shows the corrosion effect after a cyclic 1008 hour aging of samples which were coated before aging at 750° C in a chlorine and sulfur dioxide-containing atmosphere with a coat of Na<sub>2</sub>SO<sub>4</sub>/KCl. This test serves to test resistance to sulfate corrosion. As can be seen in the figure, the degrees of corrosion in the alloys according to the invention are markedly lower also with this corrosion stress than the alloy 2,4856 used at this time under such corrosion conditions.

[0018] The outstanding characteristics of the alloy according to the invention can be attributed to the silicon additions and to the coordination of the alloy elements molybdenum, chromium and iron. The silicon contents of the alloy according to the invention should be between 0.6 and 1.7 %, since the corrosion-inhibiting effect of silicon no longer occurs with lower silicon contents and since embrittling silicides and a marked loss in ductility, in particular at middle temperatures (500 - 800°C) are to be expected with higher contents in silicon. With silicon contents between 0.5 and 1.7 % the notch bar test toughness, measured in ISO-V Charpy tests, does not drop below 100 J/cm as shown in Fig. 5, even after aging for 1000 hours at 600°C.

[0019] The molybdenum content of the alloy according to the invention is limited to 10% because, as shown in Fig. 4, the vulnerability to sulphate corrosion increases with molybdenum contents. A minimum molybdenum content is required in order to avoid wet corrosion in case of

a drop below the dew point.

[0020] The chromium content of the alloy according to the invention should be between 18% and 22% in order to ensure sufficient corrosion resistance. Greater contents in chromium render the workability of nickel-chromium-molybdenum alloys markedly more difficult.

[0021] The alloy should furthermore contain hafnium and/or rare earth elements and/or zirconium and/or yttrium if an improved adherence of protective oxide layers is required in case of rapid temperature changes for specific applications, e.g. in automobile exhaust systems. However the sum of these reactive elements should not exceed 0.5%.

[0022] The iron content of the alloy according to the invention is limited to a maximum of 5%, as the danger that slightly volatile iron chlorides may be produced exists in case of higher iron contents. A minimum iron content of 1% is however required in order to ensure the workability of the alloy.

[0023] The carbon content of the alloy according to the invention is limited to a maximum 0.05% because of the danger of intercrystalline corrosion in case of higher carbon contents.

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[0024] The contents of titanium and aluminum are limited for either to a maximum of 0.5% and the actually undesirable contents of niobium to a maximum of 0.5% as these elements may lead to a loss of ductility at medium temperatures because of the formation of intermettallic phases. The total sum of additions of niobium, aluminum and titanium should not exceed 1%. A minimum content in oxygen-refined elements aluminum, titanium, magnesium and calcium is however necessary in order to ensure good oxidation resistance. The contents in manganese should be at least 0.05% for processing reasons, but should not exceed 0.5% because higher manganese contents adversely affect the oxidation resistance. In order to improve workability, 0.001 to 0.01% boron are also added to the alloy.

[0025] The contents in phosphor and sulfur should be kept as low as possible, as these interfacially active elements lower the high-temperature corrosion resistance as well as the ductility of the alloy.

[0026] The alloy according to the invention can be used for bands, foils, sheets, pipes (seamless or welded), wires, as application weldment, as application plating or as composite piping.

[0027] The production of the alloy according to the invention may be effected by means of block casting or also continuous casting after melting in a vacuum induction furnace or after

open melting. The alloy may be remelted but this is not absolutely necessary. Hot-forming is effected by forging, hot rolling or extruder, while cold forming is effected by cold rolling, wire pulling or putting through a pilger mill. The production of combination materials, e.g. plating on carbon steel, can be done by means of one of the conventional application welding processes, through cold or hot rolling of sheets or bands, through explosive cladding or through one of the conventional processes for the production of bimetal pipes.

**[0028]** Thanks to its excellent resistance to chlorination, the alloy is especially suitable in form of band or sheet, pipe or plating material for utilization in hot, chlorine-containing gases, or in the presence of chloride-containing coatings, such as occur in chemical industrial plants, in plants for the thermal treatment of chlorine-containing chemical waste and contaminated soil as well as in car exhaust gas systems (bellows for the uncoupling of exhaust catalytic converter and engine). The excellent resistance of the alloy to complex corrosive salt deposits (boiler ash) renders the alloy also suitable for the utilization as plating and construction material in plants for thermal waste removal, in large diesel engines, in plants for the obtention of energy from biomass and in plants of the cellulose industry.

CLAIMS

1. Austenitic nickel-chromium-molybdenum alloys with additions of silicon, characterized by alloy components (in mass percentages) :

Cr	18 - 22 %
Mo	6 - 10 %
Si	0.6 - 1.7 %
C	0.002 - 0.05 %
Fe	1 - 5 %
Mn	0.05 - 0.5 %
Al	0.1 - 0.5 %
Ti	0.1 - 0.5 %
Mg	0.005 - 0.05 %
Ca	0.001 - 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 - 0.01 %
Cu	max. 0.5 %
Co	max 1 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.02 - 0.5%

the remainder being nickel and impurities caused by the melting process, whereby the total amount of additions in Nb + Al + Ti do not exceed 1 %.

2. Alloy as in claim 1, characterized by alloy components (in mass percentages):

Cr	18 - 20 %
Mo	8 - 9.0 %
Si	0.7 - 1.1 %
C	0.002 - 0.15 %
Fe	2.5 - 3.5 %
Mn	0.05 - 0.1 %
Al	0.1 - 0.3 %

Ti 0.1 - 0.4 %  
Mg 0.005 - 0.15 %  
Ca 0.001 - 0.005 %  
V max. 0.1 %  
P max. 0.002 %  
S max. 0.001 %  
B 0.001 - 0.001 %  
Cu max. 0.5 %  
Nb max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.03 - 0.06%  
the remainder being nickel and impurities caused by the melting process.

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3. Alloy as in claim 1, characterized by a molybdenum content between 6.5 and 9.5 %
  4. Alloy as in claim 1, characterized by a silicon content between 0.6 and 1.3 %
  5. Utilization of the alloy as in one of the claims 1 to 4, for the production of pipes, sheet metal, band material, foils, wires as well as of items made of these semi-products.
  6. Utilization of the alloy according to one of the claims 1 to 4 for the production of composite pipes.
  7. Utilization of the alloy according to the invention as in one of the claims 1 to 4 as corrosion protection in form of applied welding or plating.



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(Substitute Specification - Marked-Up Version)

**AUSTENITIC NICKEL-CHROMIUM-MOLYBDENUM-SILICON ALLOY WITH  
HIGH CORROSION RESISTANCE TO HOT CHLORIDE-CONTAINING GASES AND  
CHLORIDE**

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[0001] The invention relates to an austenitic nickel-chromium-molybdenum-silicon alloy with additions of silicon.

[0002] In plants and aggregates where hot chlorine-containing gases and chloride-containing deposits occur (chemical plants, thermal waste-disposal facilities, in particular when recycling special waste, plants for the recycling of biomass, large diesel engines, exhaust systems of automobiles) ferritic boiler construction steel is used at temperatures up to 400°C. At higher temperature, nickel-chromium-molybdenum alloys with 21.5% chromium, 9% molybdenum, 3.7% niobium 2.5% iron, and the remainder nickel and unavoidable impurities (German material number 2.4856) are used (steel code 1995)

[0003] [However, the] The alloy with the material number 2.4856 is however difficult to process. [Furthermore] In addition this alloy suffers a considerable ductility loss at temperatures above 500°C, a loss which may result in the formation of cracks in pressure-carrying components

and/or those subjected to heavy mechanical stress. To a certain extent, the start of precipitation of the ductility-reducing precipitation [precipitants] can be delayed by lowering the iron content.

[0004] Measures leading to a clear rise in ductility are indicated in the international patent application WO 95/31579 in which a new alloy is described on basis of the alloy according to material number 2.4856 which [that] distinguishes itself through increased hot and cold formability and a greater ductility.

[0005] [Also the] The new alloy described in this publication still has some disadvantages. Thus the indicated ductility-raising measures cause the corrosion resistance to gases containing great amounts of chlorine and coatings containing chloride to drop below that of alloy with the material number 2.4856. Already with this alloy, high corrosion rates occur for reasons of constantly rising process and exhaust gas temperatures due to the increase in effectiveness. Alloys of the type 2.4856 are [furthermore] in addition subject to heat corrosion by [sulfate] sulphate-containing deposits, so that a considerable need for an alloy of a different type, with improved resistance to high-temperature corrosion exists.

[0006] JP-A 6199649 discloses an alloy for electrically conductive rollers whose essential alloy components (in weight percentages) are indicated as follows: Cr 15 - 30%, Mo 4 - 10%, Si  $\leq$  2, Fe  $\leq$  10 %, Mn  $\leq$  2 %, Al 0.2 - 2 % and Ti 0.05 - 2 %. Alternatively, Niob can also

be used instead of Titan in the above-mentioned distribution.

[0007] WO-A 8901985 discloses a corrosion-resistant cast alloy which (in weight %) contains essentially the following alloy components: Cr 20 - 25 %, Mo 6 - 9 %, Si 05 - 1 %, Fe 15 - 20 % and Mn 2 - 4 %. In addition a high addition of Co, in the amount of 4 - 8% is indicated.

[0008] It is the object of present invention to develop an alloy with a resistance to chlorine [chloric] gas corrosion and to chloride-containing coatings [clearly in proved over] significantly superior to that of the state of the art, while [having] at the same time [better] providing increased resistance to [sulfate] sulphate corrosion [and a] while possessing high ductility over the entire temperature range up to 1000°C.

[0009] [This] The object is attained by means of a silicon-containing nickel-chromium-molybdenum alloy which is made up of the following components (in mass %):

Cr	18 - 22 %
Mo	6 - 10 %
Si	0.6 - 1.7 %
C	0.002 - 0.05 %
Fe	1 - 5 %
Mn	0.05 - 0.5 %
Al	0.1 - 0.5 %
Ti	0.1 - 0.5 %
Mg	0.005 - 0.05 %

Ca 0.001 - 0.01 %

V max. 0.5 %

P max. 0.02 %

S max. 0.01 %

B 0.001 - 0.01 %

Cu max. 0.5 %

Co max 1 %

Nb max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.02 - 0.5%

the remainder being nickel and impurities caused by the melting process, whereby the total amount of additions in Nb + Al + Ti do not exceed 1 %.

[0010] Advantageous further developments of the object of the invention are to be found in the sub-claims.

[0011] The alloy according to the invention is clearly more high-temperature corrosion resistant to [high temperature corrosion from] chlorine-containing gases, [chlorine] chloride- containing ash[es], deposits and salt compounds [combinations] than those of [in] the state of the art, while [being] at the same time being corrosion resistant to [sulfate] sulphate corrosion and wet corrosion [while remaining] and is at the same time highly ductile.

[0012] [Advantageous further developments of the object of the invention are to be found in the sub-claims.]

[0013] A preferred alloy is composed of [characterized by] the following alloy

components (in mass percentages) :

Cr	18 - 20 %
Mo	8 - 9.0 %
Si	0.7 - 1.1 %
C	0.002 - 0.15 %
Fe	2.5 - 3.5 %
Mn	0.05 - 0.1 %
Al	0.1 - 0.3 %
Ti	0.1 - 0.4 %
Mg	0.005 - 0.15 %
Ca	0.001 - 0.005 %
V	max. 0.1 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 - 0.001 %
Cu	max. 0.5 %
Nb	<u>max. 0.5 %</u>
Hf and/or Y and/or Zr and/or rare earth <u>elements</u> - 0.03 - 0.06%	
the remainder being nickel and impurities caused by the melting process.	

[0014] The alloy is advantageously suited on the one hand for the production of pipes, in particular composite pipes, sheet metal, band material, [films] foils, wires as well as [articles] items made from these semi-[finished]products, and [on the other hand for build-up] is furthermore suitable as corrosion protection in form of applied welding or plating [of applied corrosion protection].

[0015] The advantageous [properties] characteristics of the alloy according to the invention [become apparent from the] appear in the following examples of embodiments

[indicated below]. Table 1 shows [the] for example [of] analyses of [charges from] batches of the alloy [(A-f)] according to the invention (A-F) as well as the comparison alloys (G, H) [with components outside] other than the combination according to the invention (G, H). [For comparison, the] The alloy 2.4856 was used for comparison. All alloy variants [of the alloy] were produced from cast blocks by means of hot rolling followed by cold rolling at room temperature.

**[0016]** The resistance of the alloy according to the invention to chloride corrosion [appears from the] is depicted in Figs. 1 and 2. For the tests, polished and cleaned test coupons of different test alloys were [dipped into] submerged in an aqueous solution of 1 mol/l NaCl, 0.1 mol/l CaCl<sub>2</sub> and [0.24] 0.25 mol/l NaHCO<sub>3</sub>, [were] dried at 60°C and then aged in the air at 750°C [air temperature] for 240 hours. This test simulates the stresses which appear [such as occur] e.g. in exhaust systems of car [automobile] engines (at [on expansion] bellows for [the] uncoupling [of] catalytic converter and engine). Fig. 1 shows the disappearance of [he] metal [loss], Fig. 2 shows the metallographically determined corrosion effect [damage determined through metallography] at the end of the test. In [these investigations] tests it was found [that] surprisingly that the resistance to chloride corrosion could be markedly improved [considerably e.g.] over that of [the] alloy 2,4856 by [adding] the addition of silicon in quantities from 0.6 and 1.7%.

[0017] The advantageous influence of silicon can also be seen [becomes apparent] in Fig. 3 which shows the metallographically determined corrosion [damage of] effect on samples [determined through metallography, said samples having been placed into] which were aged in a complex medium (chlorine-containing synthetical waste combustion gas ( $2.5 \text{ g/m}^3 \text{ HCl}$ ,  $1.3 \text{ g/m}^3 \text{ SO}_2$ / 9%  $\text{O}_2$ , the remainder [ $\text{N}_s$ ]  $\text{N}_2$ ) [with simultaneous subjection to] while at the same time adding chloride-containing boiler ash) for over 1000 hours at  $600^\circ \text{C}$ . By comparison [Compared] with the [charge containing little silicon] low-silicon batch (e.g. G) the [silicon-containing] alloy containing silicon according to the invention [suffers distinctly] suffered markedly less corrosion [attack] effect.

[0018] Fig. 4 shows the corrosion [damage] effect after a cyclic 1008 [hours of cyclical] hour aging of samples which [had been] were coated [with a coating consisting of  $\text{Na}_2\text{SO}_4/\text{KCl}$ ] before aging at  $750^\circ \text{C}$  in a chlorine and sulfur dioxide-containing atmosphere with a coat of  $\text{Na}_2\text{SO}_4/\text{KCl}$ . This test serves to test [the] resistance to sulphate corrosion. As can be seen in the figure, the degrees of corrosion in the alloys according to the invention [has clearly] are markedly lower [corrosion rates] also with this corrosion stress [exposure to corrosion] than the alloy 2,4856 used at this time under such corrosion conditions [of corrosion].

[0019] The outstanding characteristics of the alloy according to the invention can be attributed to the silicon additions and to the coordination of the alloy elements molybdenum,

[chrome] chromium and iron. The silicon contents of the alloy according to the invention should be [from] between 0.6 [to] and 1.7 %, since the corrosion-[resistant] inhibiting effect of [the] silicon no longer occurs with lower silicon contents[,], and since [greater contents of silicon result in the appearance of] embrittling silicides and a [distinct] marked loss [of] in ductility, in particular at middle temperatures [in the middle range] (500 - 800°C) are to be expected with higher contents in silicon. With silicon contents [from] between 0.5 [to] and 1.7 % the [notched] notch bar [impact value] test toughness, measured [on] in ISO-V [notched bar samples] Charpy tests, does not drop below 100 J/cm as shown in Fig. 5, even after aging for 1000 hours [aging] at 600°C [, as shown in Fig. 5].

[0020] The molybdenum content of the alloy according to the invention is limited to 10% [since] because, as shown in Fig. 4, the [risk] vulnerability to [sulfate] sulphate corrosion increases with [higher] molybdenum contents. A minimum molybdenum [Molybdenum] content is [necessary] required in order to avoid wet corrosion in case of [falling short of] a drop below the dew point.

[0021] The [chrome] chromium content of the alloy according to the invention should be between 18% and 22% in order to ensure sufficient corrosion resistance. Greater [Higher chrome] contents in chromium render the workability of nickel-[chrome]chromium-molybdenum alloys [distinctly] markedly more difficult.



[0022] [In addition, the] The alloy should furthermore contain hafnium and/or rare earth elements and/or zirconium and/or yttrium if an improved [adhesion] adherence of protective oxide layers is required in case of rapid temperature changes for specific applications, e.g. in [the] automobile exhaust systems [at high temperatures and/or in case of rapid temperature changes]. [The] However the sum of these reactive elements should [however] not exceed 0.5%.

[0023] The iron content[s] of the alloy according to the invention is limited to a maximum of 5%, [since] as the danger that slightly volatile iron chlorides may be produced exists in case of higher iron contents [involve the danger of easily volatile iron chlorides being formed]. A minimum iron content of 1% is however required in order to ensure the workability of the alloy.

[0024] The carbon content of the alloy according to the invention is limited to a maximum 0.05% [as higher carbon contents involve the risk] because of the danger of intercrystalline corrosion in case of higher carbon contents.

[0025] The contents of titanium and aluminum [contents] are limited for either [respectively] to a maximum of 0.5%[;] and the actually undesirable contents of niobium [is limited] to a maximum of 0.5% [because] as these elements may [result in] lead to a loss of ductility at medium temperatures [due to] because of the formation of intermettallic phases. The

total sum of additions of niobium, aluminum and titanium [additives] should not exceed 1%. A minimum content in oxygen-[affinitive]refined elements aluminum, titanium, magnesium and calcium is however necessary in order to ensure good [resistance to] oxidation resistance. The contents in manganese [content] should be at least 0.05% for processing reasons, but should not exceed 0.5% because higher [contents in] manganese contents adversely affect [have an unfavorable effect on] the oxidation resistance [to oxidation]. In order to [To] improve workability, 0.001 to 0.01% boron are also added [into the mix] to the alloy.

[0026] The contents in phosphor and sulfur [contents] should be kept as low as possible, as [because] these [surface] interfacially active elements lower [reduce] the high-temperature corrosion resistance [at high temperature] as well as the ductility of the alloy.

[0027] The alloy according to the invention can be used for bands, [films] foils, [sheet metals] sheets, pipes (seamless or welded), wires, [for applied welding, applied] as application weldment, as application plating or as composite piping.

[0028] The production of the alloy according to the invention [can be produced by ingot] may be effected by means of block casting [as well as by] or also continuous casting after [following] melting in a vacuum induction furnace or after open melting. The [Recasting of the] alloy [is possible] may be remelted but this is not absolutely necessary. Hot-forming is

[achieved] effected by forging, hot rolling or [continuous pressing and] extruder, while cold forming is effected by cold rolling, wire pulling or [by means of] putting through a pilger mill. The production of [composite] combination materials, e.g. plating on carbon steel, can be [effected] done by means of one of the [customary] conventional application welding processes, [by] through cold or hot rolling of [sheet metal] sheets or bands, [by] through explosive cladding or [bu] through one of the [customary] conventional processes for [in] the production of bimetal pipes.

**[0029]**        Thanks [Due] to its excellent resistance to chlorination, the alloy is especially [well suited as] suitable in form of band [and] or sheet [metal], pipe or plating material for utilization in hot, chlorine-containing gases, or in the presence of chloride-containing coatings, such as occur in chemical industrial plants, in plants for the thermal treatment [plants for] of chlorine-containing chemical waste and contaminated [floors] soil as well as in [automobile] car exhaust gas systems ([expansion] bellows for the uncoupling of exhaust catalytic converter and engine). The excellent resistance of the alloy to complex corrosive [saline] salt deposits (boiler [furnace] ash) renders the alloy also suitable for the utilization as plating and construction material in plants for thermal waste removal [removal plants], in large diesel engines [motors], in plants for the obtention of energy from biomass and in plants of the cellulose industry.

CLAIMS

1. Austenitic nickel-chromium-molybdenum alloys with [additives] additions of silicon, characterized by alloy components (in mass percentages) :

Cr	18 - 22 %
Mo	6 - 10 %
Si	0.6 - 1.7 %
C	0.002 - 0.05 %
Fe	1 - 5 %
Mn	0.05 - 0.5 %
Al	0.1 - 0.5 %
Ti	0.1 - 0.5 %
Mg	0.005 - 0.05 %
Ca	0.001 - 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 - 0.01 %
Cu	max. 0.5 %
Co	max 1 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.02 - 0.5%  
the remainder being nickel and impurities caused by the melting process, whereby the total amount of additions in Nb + Al + Ti do not exceed 1 %.

2. Alloy as in claim 1, characterized by alloy components (in mass percentages):

Cr	18 - 20 %
Mo	8 - 9.0 %
Si	0.7 - 1.1 %
C	0.002 - 0.15 %
Fe	2.5 - 3.5 %
Mn	0.05 - 0.1 %
Al	0.1 - 0.3 %

Ti 0.1 - 0.4 %  
Mg 0.005 - 0.15 %  
Ca 0.001 - 0.005 %  
V max. 0.1 %  
P max. 0.002 %  
S max. 0.001 %  
B 0.001 - 0.001 %  
Cu max. 0.5 %  
Nb max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.03 - 0.06%  
the remainder being nickel and impurities caused by the melting process.

3. Alloy as in claim 1, characterized by a molybdenum content between 6.5 and 9.5 %
4. Alloy as in claim 1, characterized by a silicon content between 0.6 and 1.3 %
5. Utilization of the alloy as in one of the claims 1 to 4, for the production of pipes, sheet metal, band material, [films] foils, wires as well as of [articles] items made of these semi-  
[finished]products.
6. Utilization of the alloy [as in] according to one of the claims 1 to 4 for the production of composite pipes.
7. Utilization of the alloy according to the invention as in one of the claims 1 to 4 as corrosion protection in form of applied [by means of bulid-up] welding or plating.

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Translation of International Application as Filed

AUSTENITIC NICKEL-CHROMIUM-MOLYBDENUM-SILICON  
ALLOY WITH HIGH CORROSION RESISTANCE TO HOT  
CHLORIDE-CONTAINING GASES AND CHLORIDE.

The invention relates to an austenitic nickel-chromium-molybdenum-silicon alloy with additions of silicon.

In plants and aggregates where hot chlorine-containing gases and chlorine-containing deposits occur (chemical plants, thermal waste-disposal facilities, in particular when recycling special waste, plants for the recycling of biomass, large diesel engines, exhaust systems of automobiles) ferritic boiler construction steel is used at temperatures up to 400 C. At higher temperatures, nickel-chromium-molybdenum alloys with 21.5% chromium, 9% molybdenum, 3.7% niobium, 2.5% iron and the remainder nickel and unavoidable impurities (German material number 2.4856) are commonly used (steel code 1995).

However the alloy with the material number 2.4856 is difficult to process. Furthermore, this alloy suffers a considerable ductility loss at temperatures above 500 C, a loss that may result in the formation of cracks in pressure-carrying components and/or those subjected to heavy mechanical stress. To a certain extent, the start of precipitation of the ductility-reducing precipitants can be delayed by lowering the iron content.

Translation of International Application as Filed

Measures leading to a clear rise in ductility are indicated in the international patent application WO 95/31579 in which a new alloy is described on basis of the alloy according to material number 2.4856 that distinguishes itself through increased hot and cold formability and a greater ductility.

Also the new alloy described in this publication still has some disadvantages. Thus the indicated ductility-raising measures cause the corrosion resistance to gases containing great amounts of chlorine and coatings containing chloride to drop below that of the alloy with the material number 2.4856. Already with this alloy, high corrosion rates occur for reason of constantly rising process and exhaust gas temperatures due to the increase in effectiveness. Alloys of the type 2.4856 are furthermore subject to heat corrosion by sulfate-containing deposits, so that a considerable need for an alloy of a different type, with improved resistance to high-temperature corrosion exists.

It is the object of the present invention to develop an alloy with a resistance to chloric gas corrosion and chloride-containing coatings clearly improved over the state of the art while having at the same time better resistance to sulfate corrosion and a high ductility over the entire temperature range up to 1000 C.

This object is attained by a silicon-containing nickel-chromium-molybdenum alloy which is made up of the following components (in mass %)

## Translation of International Application as Filed

Cr	18 – 22 %
Mo	6 – 10 %
Si	0.6 – 1.7 %
C	0.002 – 0.05 %
Fe	1 – 5 %
Mn	0.05 – 0.5 %
Al	0.1 – 0.5 %
Ti	0.1 – 0.5 %
Mg	0,005 – 0.05 %
Ca	0.001 – 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 – 0.01 %
Cu	max. 0.5 %
Co	max. 1 %

Hf and/or Y and/or Zr and/or rare earth : 0.02 – 0.5%, the remainder being nickel and impurities caused by the melting process.

The alloy according to the invention is clearly more resistant to high-temperature corrosion from chloride-containing gases, chlorine-containing ashes, deposits and salt combinations than in the state of the art while being at the same time corrosion-resistant to sulfate corrosion and wet corrosion while remaining highly ductile.



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Advantageous further developments of the object of the invention are found in the sub-claims.

A preferred alloy is characterized by the following alloy components (in mass %):

Cr	18 – 20 %
Mo	8 – 9 %
Si	0.7 – 1.1 %
C	0.02 – 0.015 %
Fe	2.5 – 3.5 %
Mn	0.05 – 0.1 %
Al	0.1 – 0.3 %
Ti	0.1 – 0.4 %
Mg	0,005 – 0.015 %
Ca	0.001 – 0.005 %
V	max. 0.01 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 – 0.001 %
Cu	max. 0.5 %

Hf and/or Y and/or Zr and/rare earth : 0.03 – 0.06%, the remainder being nickel and impurities caused by the melting process.

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The alloy is advantageously suited on the one hand for the production of pipes, in particular composite pipes, sheet-metal, band material, films, wires as well as articles made from these semi-finished products and on the other hand for build-up welding or plating of applied corrosion protection.

The advantageous properties of the alloy according to the invention become apparent from the examples of embodiments indicated below Table 1 shows the example of analyses of charges from the alloy (A-F) according to the invention as well as the comparison alloys (G, H) with components outside the invention. For comparison, the alloy 2.4856 was used. All variants of the alloy were produced from cast blocks by hot rolling followed by cold rolling at room temperature.

The resistance of the alloy according to the invention to chloride corrosion appears from the figs. 1 and 2. For the tests, polished and cleaned test coupons of different test alloys were dipped into an aqueous solution of 1 mol/l NaCl, 0.1 mol/l CaCl<sub>2</sub> and 0.24 mol/l NaHCO<sub>3</sub>, were dried at 60 °C and then aged at 750 °C air temperature for 240 hours. This test simulates the stresses such as occur e.g. in exhaust systems of automobile engines (on expansion bellows for the uncoupling of catalytic converter and engine). Fig. 1 shows the metal loss, Fig. 2 shows the corrosion damage determined through metallography at the end of the test. In these investigations it was found that surprisingly the resistance to chloride corrosion could be improved considerably e.g. over the alloy 2.4856 by adding silicon in quantities from 0.6 to 1.7 %.

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The advantageous influence of silicon also becomes apparent in Fig. 3 which shows the corrosion damage of samples determined through metallography, said samples having been placed into a complex medium (chlorine-containing synthetic waste combustion gas ( $2.5 \text{ g/m}^3 \text{ HCl}$ ,  $1.3 \text{ g/m}^3 \text{ SO}_2$ / 9 %  $\text{O}_2$ , the remainder  $\text{N}_s$ ) with simultaneous subjection to chloride-containing boiler ash) for over 1000 hours at 600 °C. Compared with the charge containing little silicon (e.g. G) the silicon-containing alloy according to the invention suffers distinctly less corrosion attack.

Fig. 4 shows corrosion damage after 1008 hours of cyclical aging of samples which had been coated with a coating consisting of  $\text{Na}_2\text{SO}_4/\text{CK1}$  before aging at 750 °C in a chlorine and sulfur dioxide containing atmosphere. This test serves to test the resistance to sulfate corrosion. As can be seen in the figure, the alloy according to the invention has clearly lower corrosion rates also with this exposure to corrosion, than the alloy 2.4856 used at this time under such conditions of corrosion.

The outstanding characteristics of the alloy according to the invention can be attributed to the coordination of the alloy elements molybdenum, chrome and iron. The silicon content of the alloy according to the invention should be from 0.6 % to 1.7 %, since the corrosion-resistant effect of the silicon no longer occurs with lower silicon contents, and since greater contents of silicon result in the appearance of embrittling silicides and a distinct loss of ductility, in particular at temperatures in the middle range (500 – 800 °C).

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With silicon content from 0.5 to 1.7% the notched bar impact value , measured on ISO V notched bar samples, does not drop below 100 J/cm even after 1000 hours aging at 600 °C, as shown in Fig. 5.

The molybdenum content of the alloy according to the invention is limited to 10 % since, as shown in Fig. 4, the risk of sulfate corrosion increases with higher molybdenum contents. Molybdenum content is necessary in order to avoid wet corrosion in case of falling short of the dew point.

The chrome content of the alloy according to the invention should be between 18 and 22% in order to ensure sufficient corrosion resistance. Higher chrome contents render the workability of the nickel-chrome-molybdenum alloys distinctly more difficult.

In addition, the alloy should contain hafnium and/or rare earth and/or zirconium and/or yttrium if improved adhesion of protective oxide layers is required for specific applications, e.g. in the automobile exhaust systems at high temperatures and/or in case of rapid temperature changes. The total of these reactive elements should however not exceed 0.5 %.

The iron contents of the alloy according to the invention is limited to a maximum of 5% since higher iron contents in chloride-containing media involve the danger of easily volatile iron chlorides being formed. A minimum content of 1 % is however required in order to ensure the workability of the alloy.

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The carbon content of the alloy according to the invention is limited to a maximum of 0.05, as higher carbon contents involve the risk of intercrystalline corrosion.

The titanium and aluminum contents are limited respectively to a maximum of 0.5 %; the actually undesirable content in niobium is limited to 0.5 % because these elements may result in a loss of ductility at medium temperatures due to the formation of intermetallic phases. The total of niobium, aluminum and titanium additives should not exceed 1 %. A minimum content in oxygen-affinitive elements aluminum, titanium, magnesium and calcium is however necessary in order to ensure good resistance to oxidation. The manganese content should be at least 0.05 % for processing reasons, but should not exceed 0.5% because higher contents in manganese have an unfavorable effect on the resistance to oxidation. To improve workability, 0.001 – 0.01 % in boron are also alloyed into the mix. The phosphor and sulfur contents should be kept as low as possible because these surface-active elements reduce the corrosion resistance at high temperatures as well as the ductility of the alloy.

The alloy according to the invention can be used for bands, films, sheet metal, pipes (seamless or welded), wires, for applied welding, applied plating or as composite pipe.

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The alloy according to the invention can be produced by ingot casting as well as by continuous casting following melting in a vacuum induction furnace or open melting. Recasting of the alloy is possible but not absolutely necessary. Hot-forming is achieved by forging, hot rolling or continuous pressing, and cold forming by cold rolling, wire pulling or by means of a pilger mill. The production of composite materials, e.g. plating on carbon steel, can be effected by means of one of the customary application welding processes, by cold or hot rolling of sheet metal or bands, by explosive cladding or by one of the customary process in the production of bi-metal pipes.

Due to its excellent resistance to chlorination, the alloy is especially well suited as band and sheet metal, pipe or plating material for utilization in hot chlorine-containing gases or in presence of chloride containing coatings, such as occur in chemical plants, in thermal treatment plants for chlorine-containing chemical waste and contaminated floors as well as in automobile exhaust systems (expansion bellows for the uncoupling of catalytic converter and engine). The excellent resistance of the alloy to complex, corrosive saline deposits (furnace ash) renders the alloy also suitable for utilization as plating and construction material in thermal waste disposal plants, in large diesel motors, in plants for the obtention of energy from biomass and in plants of the cellulose industry.

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## CLAIMS

1. Austenitic nickel-chromium-molybdenum alloy with additives of silicon, characterized by the alloy components (in mass %)

Cr	18 – 22 %
Mo	6 – 10 %
Si	0.6 – 1.7 %
C	0.002 – 0.05 %
Fe	1 – 5 %
Mn	0.05 – 0.5 %
Al	0.1 – 0.5 %
Ti	0.1 – 0.5 %
Mg	0,005 – 0.05 %
Ca	0.001 – 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 – 0.01 %
Cu	max. 0.5 %
Co	max. 1 %

Hf and/or Y and/or Zr and/or rare earth : 0.02 – 0.5%, the remainder being nickel and impurities caused by the melting process.

2. Alloys as in claim 1, characterized by the alloy components (in mass %)

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Cr	18 – 20 %
Mo	8 – 9 %
Si	0.7 – 1.1 %
C	0.02 – 0.015 %
Fe	2.5 – 3.5 %
Mn	0.05 – 0.1 %
Al	0.1 – 0.3 %
Ti	0.1 – 0.4 %
Mg	0,005 – 0.015 %
Ca	0.001 – 0.005 %
V	max. 0.01 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 – 0.001 %
Cu	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth : 0.03 – 0.06%, the remainder being nickel and impurities caused by the melting process.

3. Alloys as in claim 1, characterized by molybdenum contents between 6.5 and 9.5 %.
4. Alloys as in claim 1, characterized by a silicon content between 0.6 and 1.3 %



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5. Utilization of the alloy as in one of the claims 1 to 4 for the production of pipes, sheet metal, band material, film, wires as well as articles made of these semi-finished products.
6. Utilization of the alloy as in one of the claims 1 to 4 for the production of composite pipes.
7. Utilization of the alloy as in one of the claims 1 to 4 as corrosion protection applied by means of build-up welding or plating.

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## ABSTRACT OF THE INVENTION

The present invention proposes an austenitic nickel-chromium-molybdenum-silicon alloy with a clearly improved resistance to chlorine-containing gases and chlorides such as occur e.g. in plants of the chemical industry, thermal waste disposal, in exhaust systems of automobiles and in diesel engines, consisting of:

Cr	18 – 22 %
Mo	6 – 10 %
Si	0.6 – 1.7 %
C	0.002 – 0.05 %
Fe	1 – 5 %
Mn	0.05 – 0.5 %
Al	0.1 – 0.5 %
Ti	0.1 – 0.5 %
Mg	0,005 – 0.05 %
Ca	0.001 – 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 – 0.01 %
Cu	max. 0.5 %
Co	max. 1 %

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Hf and/or Y and/or Zr and/or rare earth : 0.02 – 0.5%, the remainder being nickel and impurities caused by the melting process.

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Table 1: Examples of Alloys

Example	Chemical Composition in %															
	Ni	Cr	Mo	Fe	Si	Nb	Ti	Mg	Al	Hf	S	P	Mn	C	O	N
A	Rest	20.6	8.8	3.1	1.7	-	0.27	0.003	0.19	0.035	0.002	0.002	0.03	0.025	0.003	0.006
B	Rest	20.6	8.8	3.03	1.3	-	0.28	0.004	0.18	0.045	0.002	0.002	0.03	0.023	0.0035	0.0040
C	Rest	20.7	8.8	3.1	1.3	-	0.26	0.005	0.17	0.051	0.003	0.002	0.03	0.026	0.003	0.0065
D	Rest	20.6	8.8	3.04	0.95	-	0.27	0.006	0.19	0.050	0.002	0.002	0.03	0.017	0.0035	0.0055
E	Rest	20.8	8.7	3.2	0.6	-	0.28	0.008	0.20	0.054	0.002	0.003	0.04	0.019	0.006	0.010
F	Rest	21.9	9.4	4.1	1.56	0.01	0.28	0.009	0.16	-	0.002	0.002	0.03	0.060	0.001	0.005
G	Rest	22.2	9.2	0.8	0.08	0.01	0.32	0.005	0.14	-	0.002	0.002	0.03	0.012	0.001	0.012
H	Rest	22.50	15.5	0.34	0.04	0.01	0.01	0.008	0.31	-	0.003	0.002	0.15	0.007	-	-
2.4856	Rest	22.25	9.18	2.53	0.07	3.44	0.22	0.006	0.12	-	0.003	0.004	0.08	0.015	-	0.017

Fig.1: Loss of mass (metal loss) after 240 hour aging of salt-subjected samples in air at 750°C

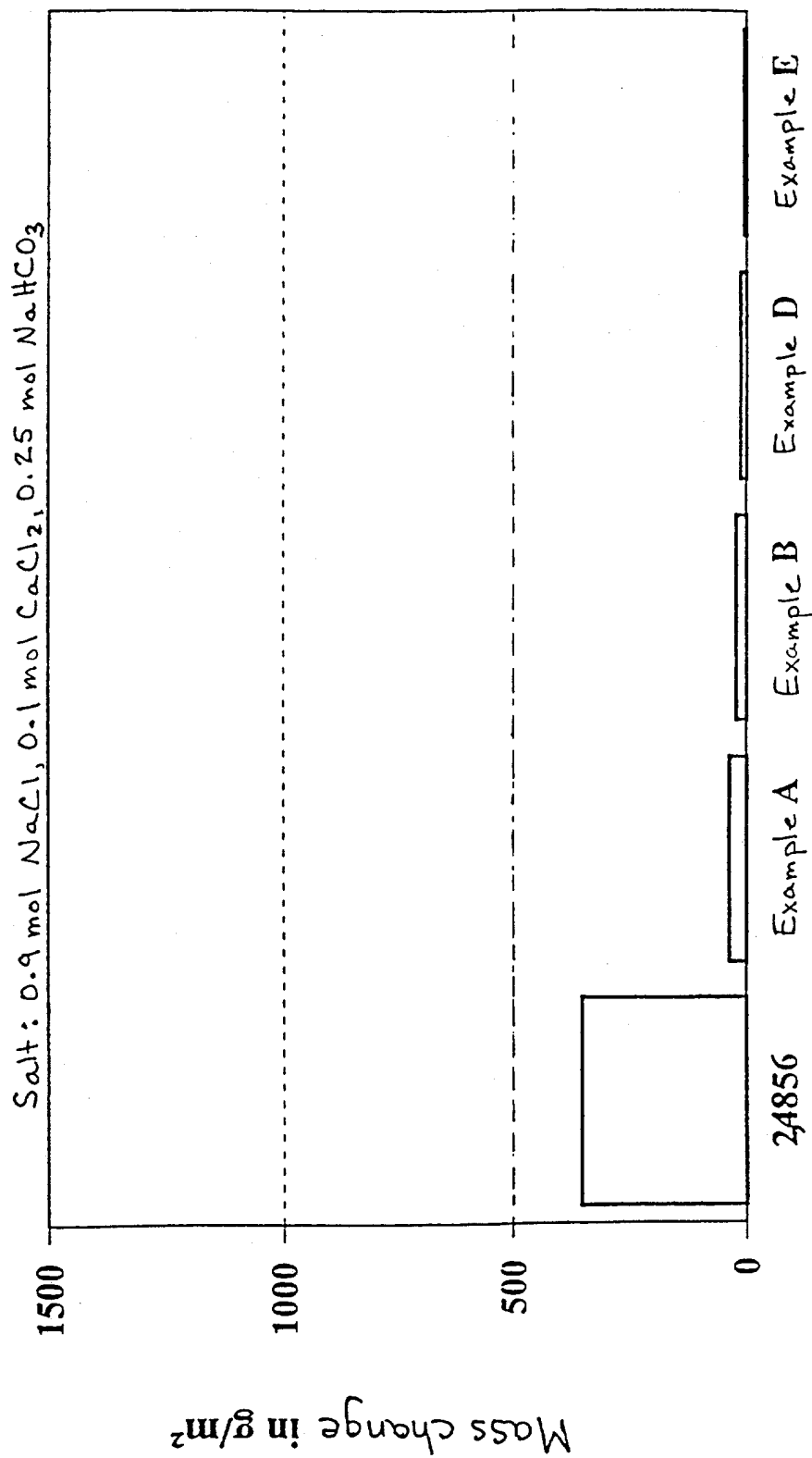


Fig.2: Metallographically determined corrosion effect after  
240 hours aging of samples subjected to salt, in air at 750°C

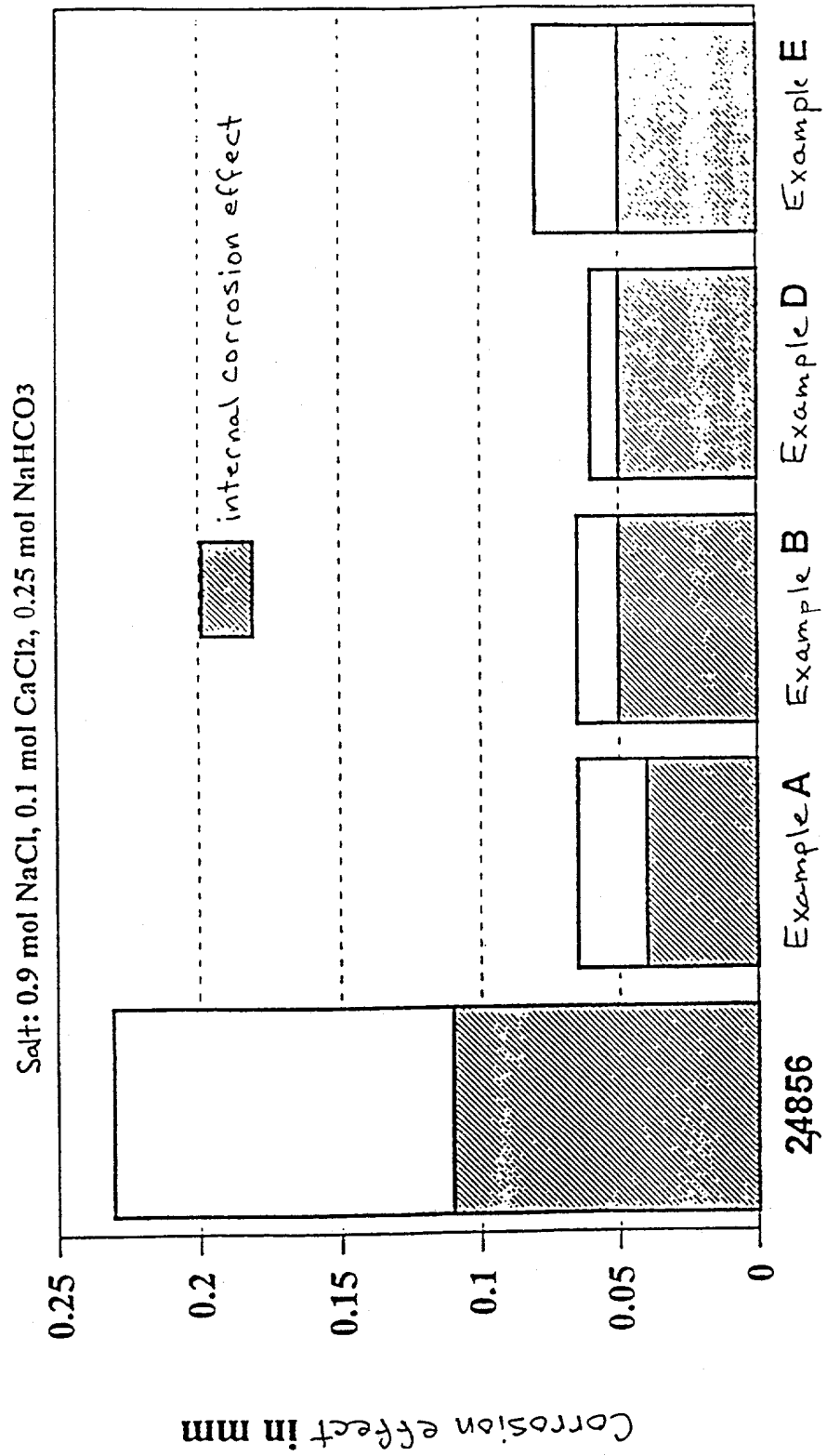


Fig.3: Internal Corrosion, metal removal and overall corrosion effect after 1000 hours of aging (600°C) in synthetic waste burning gas

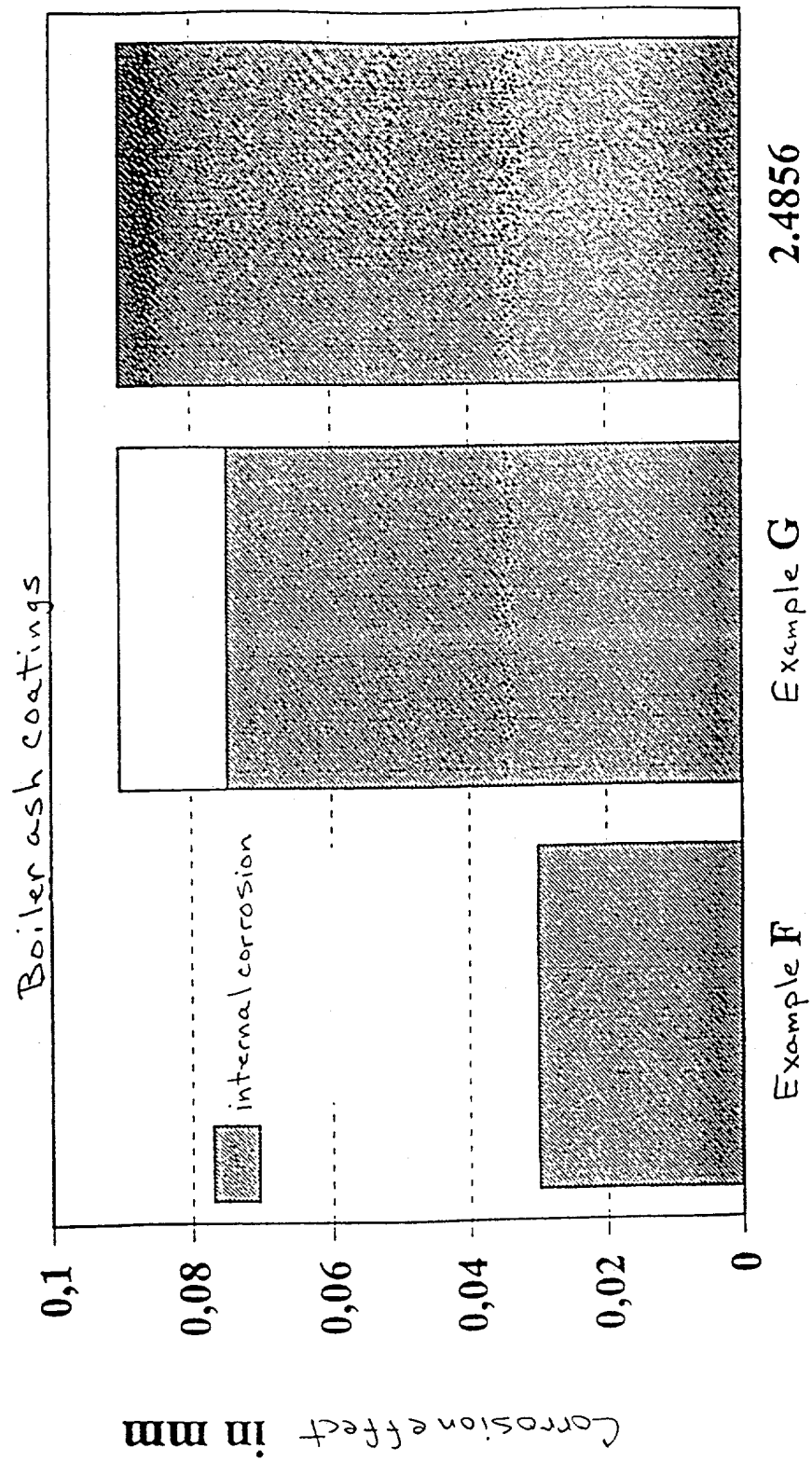


Fig.4: Overall corrosion effect after 1008 hours aging at 750°C  
in synthetic waste burning gas; Samples coated  
with Na<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>l (750°C)

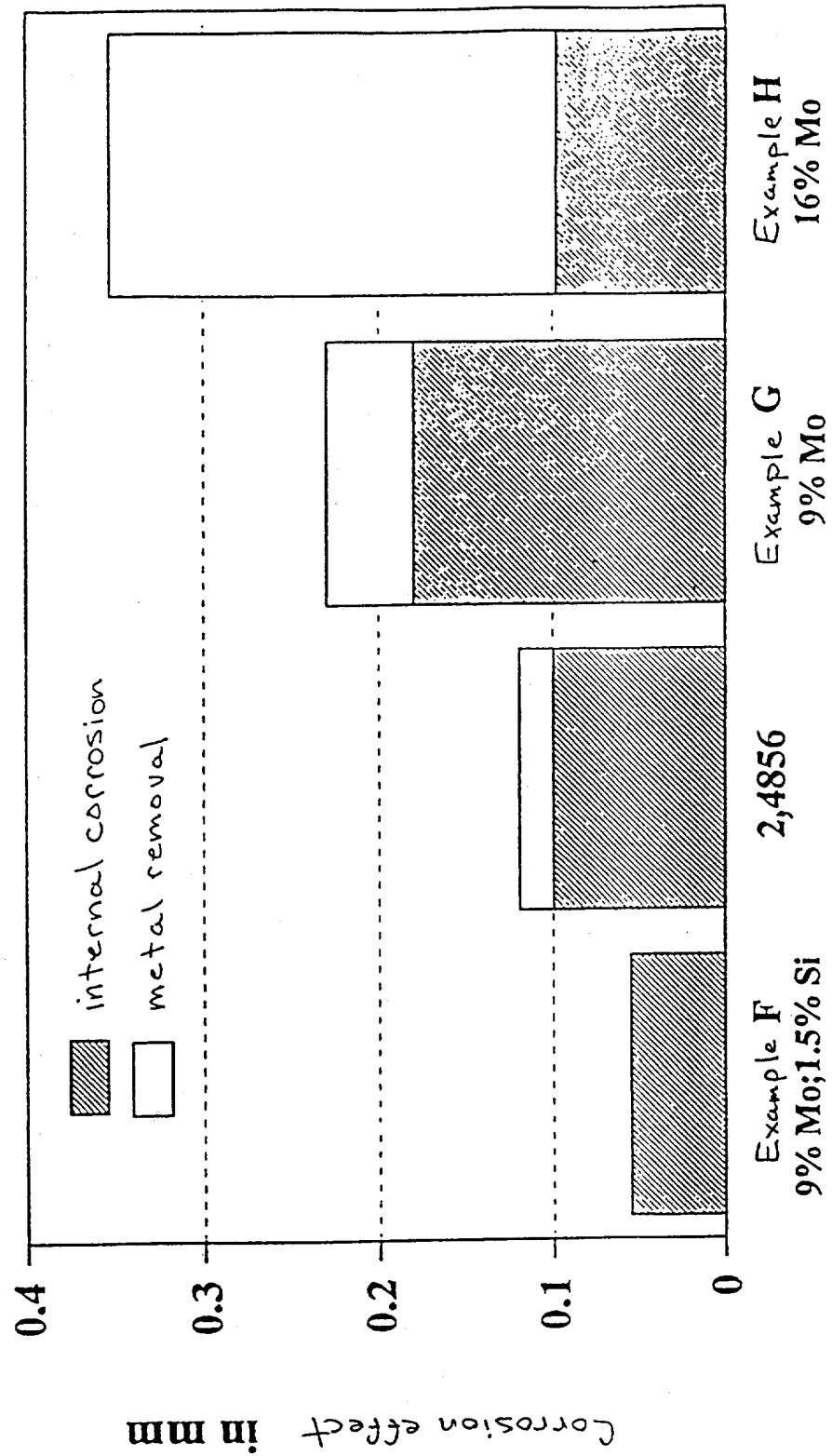
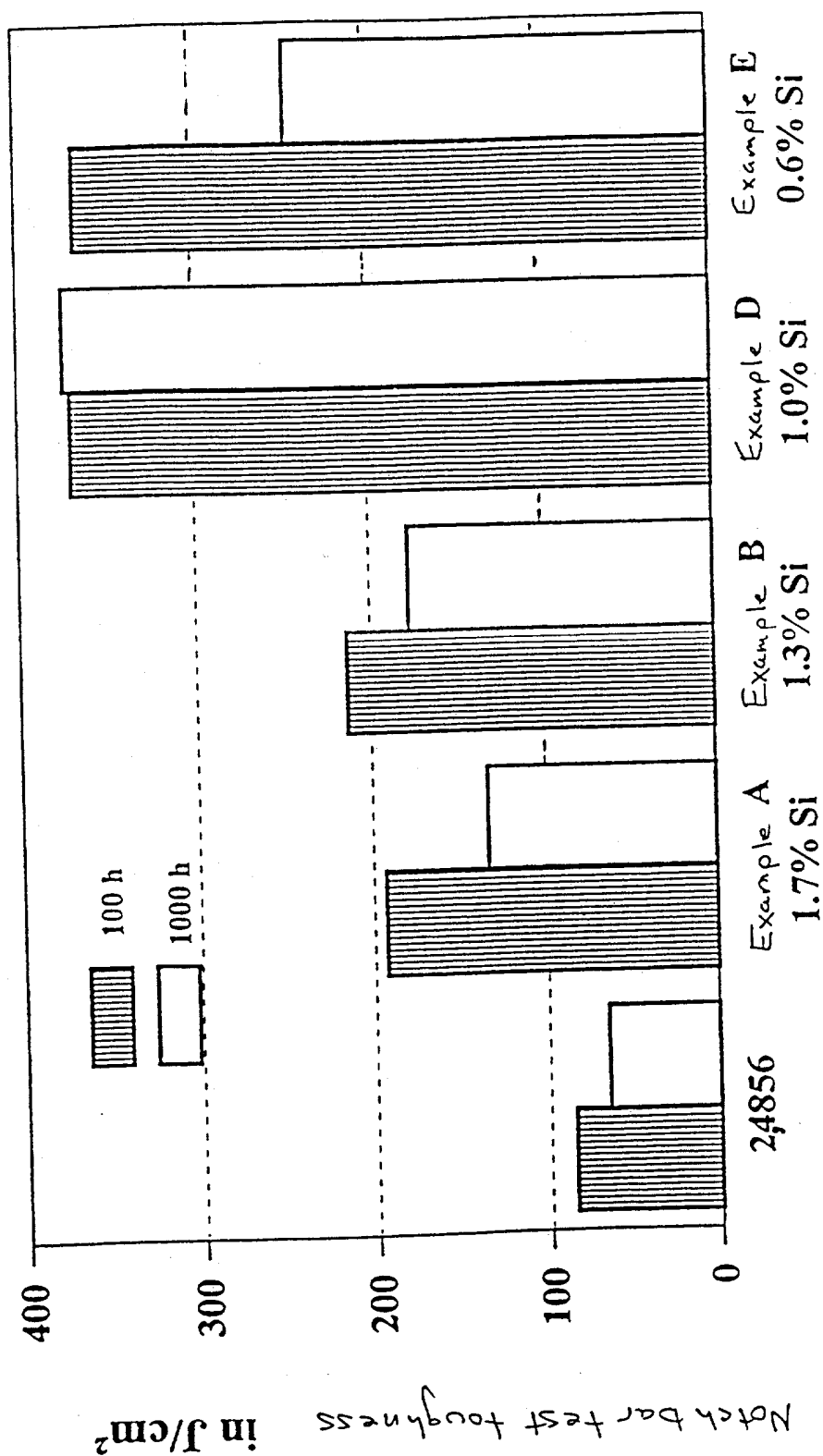




Fig.5: Notch bar test toughness of Ni-20Cr-9Mo-Si alloys after aging in air at 600°C



DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

AUSTENTIC NICKEL-CHROMIUM-MOLYBDENUM-SILICON  
ALLOY WITH HIGH CORROSION RESISTANCE TO HOT  
CHLORIDE-CONTAINING GASES AND CHLORIDE

the specification of which is attached hereto unless the following box is checked:

☒ was filed on November 26, 1997 as United States Application Number or PCT International Application Number PCT/EP97/06592 and was amended on April 16, 1999 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified, by checking the box, any foreign application for patent or inventor's certificate, or PCT International Application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s) Priority Not Claimed

<u>197 03 035.1</u>	<u>Germany</u>	<u>29 / 01 / 1997</u>	_____
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I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

_____	_____
(Application Number)	(Filing Date)

093542-072890

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

_____ (Application Number)	_____ (Filing Date)	_____ (Status--patented, pending, abandoned)
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I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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